

Phosphate Reactions as Mechanisms of High-Temperature Lubrication

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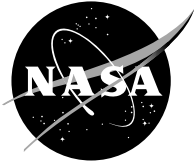
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Summary

One of the major problems preventing the operation of advanced gas turbine engines at higher temperatures is the inability of currently used liquid lubricants to survive at these higher temperatures under friction and wear conditions. Current state-of-the-art organic liquid lubricants rapidly degrade at temperatures above 300 °C; hence some other form of lubrication is necessary. Vapor-phase lubrication is a promising new technology for high-temperature lubrication. This lubrication method employs a liquid phosphate ester that is vaporized and delivered to bearings or gears; the vapor reacts with the metal surfaces, generating a solid lubricious film that has proven very stable at high temperatures. In this study, solid lubricious films were grown on cast-iron foils in order to obtain reaction and diffusion rate data to help characterize the growth mechanism. A phenomenological mathematical model of the film deposition process was derived incorporating transport and kinetic parameters that were coupled to the experimental data. This phenomenological model can now be reliably used as a predictive and scale-up tool for future vapor-phase lubrication studies.

Introduction

In the design of advanced jet engines, whose operating temperatures often exceed 400 °C, the choice of a lubricant and lubrication technique is of considerable concern. The method chosen to lubricate the contact surfaces must be effective in reducing friction and wear and increasing the usable life of these components. Materials employed to reduce friction and control wear may be in the forms of gases, solids or liquids. Gas lubricants find most of their applications in bearing technology. The drawback of such bearings is their relatively low load-carrying capacity. Solid lubricants can reduce friction and wear, but the lubricating films are slowly consumed as surface layers are sheared away, and they possess higher friction coefficients than liquid lubricants. Liquid lubricants provide excellent protection at low temperatures, but at temperatures above 300 °C even the most advanced liquid lubricants degrade rapidly and cannot be used over extended times. Because of the thermal limitations exhibited by conventional liquid lubricants, vapor-phase lubrication (VPL) has received a great deal of attention over the past decade as an alternative approach for high-temperature lubrication. The majority of VPL studies have utilized a liquid phosphate ester that is transported as a vapor to bearings or gears where the vapor reacts on the metal surfaces generating a solid lubricious film. Vapor-phase lubrication studies on a variety of metallic and ceramic substrates have indicated the need for a transition metal, such as iron, to be present in order for a film to be produced successfully (refs. 1 to 3). The chemical reaction between the organic vapor and iron-containing surfaces produces an iron-phosphate-type film (ref. 4) containing iron, phosphorus, oxygen, and carbon. This method has been successfully applied to metals at high temperatures (refs. 5 to 7). Makki and Graham (ref. 6) studied tricresyl phosphate (TCP) and postulated a mechanism for vapor-phase deposition of TCP on different surfaces including metals, quartz, and ceramics to produce tenacious solid films with a nodular structure. While their studies and results were exciting, the ortho isomer of TCP is a known neurotoxin, and it can thermally decompose further into

neurotoxic compounds when combined with other lubricants. Aiming to overcome the potential dangers associated with TCP, Rao (ref. 7) investigated an alternative vapor-phase lubricant called bis-(4-fluorophenoxy)-tetrakis-(3-trifluoromethylphenoxy) cyclotriphosphazene also referred to as X-1P. X-1P provided adequate lubrication and was shown to work at temperatures higher than those used for TCP. However, at high temperatures X-1P forms hydrogen fluoride and corrodes metallic parts over extended operation.

In response to health and environmental concerns, “synthetic” analogues to the natural phosphate esters were developed to reduce both toxicological concerns and production costs. Because of its chemical similarity with TCP (figs. 1 and 2), the alternative lubricant used for this research was the phosphate ester, tert-butylphenyl phosphate (TBPP). Phosphate esters in the vapor phase have shown that, under the right conditions, they can produce a lubricating film that is stable at very high temperatures (refs. 2, 3, and 8). This film provides lubrication and has the ability to significantly reduce the coefficient of friction for operating temperatures above 300 °C. This particular feature of TBPP was recently demonstrated by Desai (ref. 8), by utilizing a universal wear tester machine (UWTM) to evaluate the performance of the lubricant under actual dynamic conditions.

The purpose of this study was the derivation and validation of a mathematical model to describe the chemical vapor deposition (CVD) of TBPP on cast iron using a modified thermogravimetric analysis (TGA) unit. Solid lubricious films were grown by CVD in the TGA unit at temperatures ranging between 260 to 330 °C. Kinetic analysis of the TGA data was used to estimate both kinetic and transport parameters to be used in the film deposition model described in this report. Surface analyses were also performed for chemical characterization of the films.

Experimental

The organic liquid used for this study was a tert-butylphenyl phosphate (TBPP) manufactured by Great Lakes Chemical Corporation (Indianapolis, IN). TBPP possesses superior oxidative, thermal, and hydrolytic stability compared to all other commercial phosphate ester products. Its extremely low volatility and exceptional stability makes TBPP an excellent choice for high-temperature applications where an ashless additive is desired. It can be an effective and highly stable antiwear additive in both petroleum and synthetic base stocks including polyesters, diesters, and polyalphaolefins. It is known to be nontoxic, and it has no halogen in its structure, which might lead to corrosion. The substrates used in these deposition experiments were cast-iron foils.

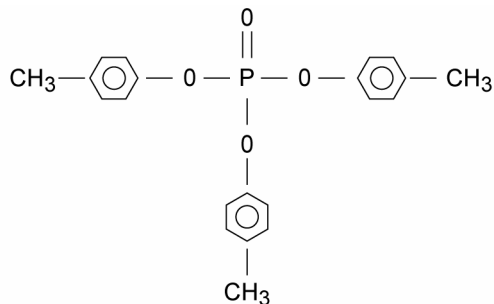


Figure 1.—Chemical structure of tricresyl phosphate (TCP).

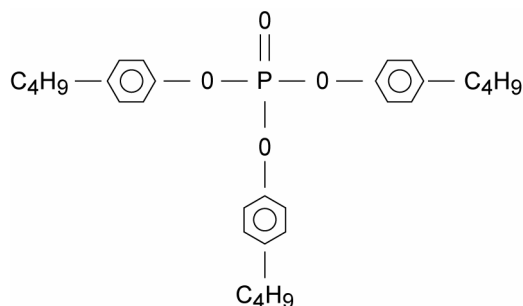


Figure 2.—Chemical structure of tert-butylphenyl phosphate (TBPP).

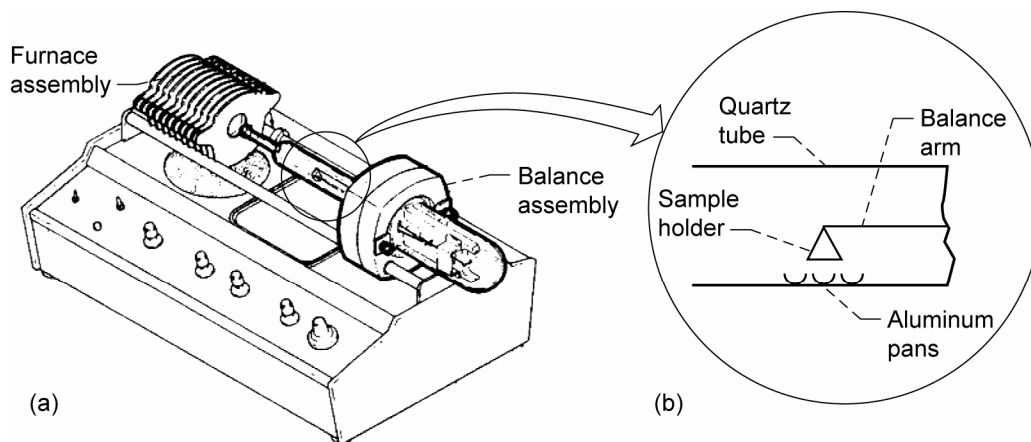


Figure 3.—DuPont instruments (Bad Homburg, Germany) 951 Thermogravimetric analyzer.
(a) TGA overview. (b) Detail of experimental setup.

The CVD experiments were performed in a TGA unit (fig. 3), modified so it would operate as a hot-wall CVD reactor. Cast-iron foil samples were shaped into cylindrical shells and suspended from a quartz rod in the TGA unit. A sample of the TBPP was placed in an aluminum pan positioned on the inside bottom of the furnace directly underneath the cast-iron foil. The amount of TBPP used was varied by using one to three pans. The location of the pans was also varied to examine the effects of location in producing thicker films. The sections of the quartz furnace tube that were not in contact with the furnace were shielded with aluminum foil to avoid or minimize TBPP condensation. No purge gas was used during the experiments in order to operate the reactor in a batch mode and maximize the conversion of the reactants inside the chamber.

The TGA unit was then programmed to slowly ramp the furnace temperature from room temperature to a preset high temperature during a 40-min period. The preset temperature, from 260 to 330 °C, was then held constant for 50 min. This 50-min isothermal time was chosen from past experience, as it proved to be sufficient to deposit films of appreciable weight at the preset temperature. After each CVD experiment, the coated cast-iron foil was removed from the TGA unit and stored for surface chemical analysis. Chemical characterization of the deposited film was carried out by elemental surface analysis using energy dispersive x-ray analysis (EDXA), Auger electron spectroscopy (AES), and Fourier transform infrared spectroscopy (FTIR).

Model Formulation

A schematic of the postulated film deposition process is shown in figure 4. The precursor, TBPP, is vaporized, and these vapors will react on contact with the surface of the cast-iron substrate, leading to the formation of an initial thin deposit. Subsequent reaction would require that the reactants diffuse through this film to reach the reaction surface. Thus the process involves three steps: (1) transportation of the TBPP species from the bulk gas to the gas-film interface, (2) diffusion through the growing film towards the substrate surface, and (3) a heterogeneous reaction between the substrate and the diffusing species.

The mathematical formulation of these steps would be

$$F_1 = k_m(C_G - C_s) \quad F_2 = -D \frac{dC}{dx} \quad F_3 = \frac{k_r C_I^n}{S_a} \quad (1)$$

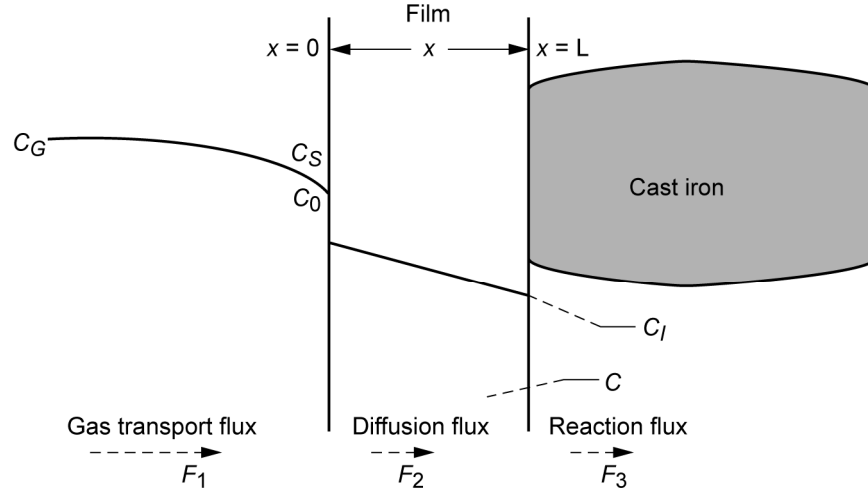


Figure 4.—Film deposition model for vapor-phase lubrication (VPL) experiments, where C is concentration of TBPP at various locations.

where the mass fluxes F_i are illustrated in figure 4. Here,

C_G	concentration of the aryl ester phosphate in the bulk gas
C_S	concentration of the aryl ester phosphate at the outermost layer of film
C_0	concentration of the aryl ester phosphate just inside the film surface
C_I	concentration of the aryl ester phosphate at the iron/film interface
D	diffusivity of the aryl ester phosphate in the film
k_m	gas phase mass transfer coefficient
k_r	rate constant for the surface chemical reaction
S_a	specific surface area (area exposed/volume of the reactor chamber)
L	film thickness
n	overall reaction order

If the diffusion characteristic time is comparatively smaller than that of the reaction, the boundaries will behave as if they were stationary on the diffusion time scale, thus enabling us to make a pseudo-steady-state approximation to simplify the governing equations; that is, diffusion and reaction are occurring in a film of constant thickness. This assumption will be validated in the next section.

Under pseudo-steady-state conditions, the mathematical model reduces to the simple diffusion model

$$\frac{d}{dx} \left(D \frac{dC}{dx} \right) = 0 \quad (2)$$

subject to the following boundary conditions:

$$\text{At } x = 0, \quad k_m (C_G - C_S) = -D \frac{dC}{dx} \quad (3)$$

$$\text{At } x = L, \quad -D \frac{dC}{dx} = \frac{k_r C_I^n}{S_a} \quad (4)$$

where $\frac{dC}{dx}$ was substituted by $\frac{(C_0 - C_I)}{L}$.

Integrating equation (2) for a constant D yields,

$$C(x) = C_0 - \left[\frac{k_r}{DS_a} C_I^n \right] x \quad (5)$$

In a typical experiment the mole fraction of TBPP in the system is significantly less than 1, making it a diluted system. Hence, the concentration just inside the film C_0 and the partial pressure P_S can be related through Henry's Law:

$$C_0 = HP_S \quad (6)$$

Where H is Henry's Law coefficient expressed as $1/RT$. Since the partial pressure of the species at the solid surface requires additional experimental information, it is expressed in terms of the species partial pressure in bulk P_G as

$$C^* = HP_G \quad (7)$$

where C^* is the concentration of the aryl ester phosphate in the film in thermodynamic equilibrium with the gas phase. Now the ideal gas law can be used to replace C_S and C_G as follows:

$$C_S = \frac{P_S}{RT} = \frac{C_0}{H} \left(\frac{1}{RT} \right) \text{ and } C_G = \frac{P_G}{RT} = \frac{C^*}{H} \left(\frac{1}{RT} \right) \quad (8)$$

Hence the pseudo-steady-state condition can be reformulated as

$$F_1 = k_m(C_G - C_S) = \frac{k_m}{HRT} (C^* - C_0) = h_G(C^* - C_0) \quad (9)$$

At steady state, $F_1 = F_2 = F_3$ and

$$h_G(C^* - C_0) = \frac{D(C_0 - C_I)}{L} = \frac{k_r C_I}{S_a} \quad (10)$$

which leads to

$$C_I^n = \frac{C^*}{\frac{1}{C_I^{n-1}} + \frac{k_r}{h_G S_a} + \frac{k_r L}{D S_a}} \quad (11)$$

where h_G is a modified gas phase mass transfer coefficient.

The rate of deposition can now be related to the growth rate of the solid film by a simple mass balance:

$$RM_w = \rho \frac{dL}{dt}, \text{ where } R = \frac{k_r C_I^n}{S_a} \quad (12)$$

Substituting equation (11) into R , the above equation becomes

$$RM_w = \rho \frac{dL}{dt} \approx \frac{dL}{dt} = \frac{M_w}{\rho S_a} \left(\frac{k_r C^*}{\frac{1}{C_I^{n-1}} + \frac{k_r L}{DS_a}} \right) \quad (13)$$

subject to $L = 0$ at $t = 0$, where $R = k_r C_I^n / S_a$ while M_w and ρ are the molecular weight and density of the film, respectively. For the typical deposition conditions, one can safely assume that the mass transfer from the gas phase to the film/substrate interface is fast as compared to the chemical reaction, and hence k_m is significantly larger than k_r ; that is,

$$\frac{k_r}{(k_m / HRT)} = \frac{k_r}{h_G} \ll 1 \quad (14)$$

Equation (13) can then be integrated, from t_0, L_0 to t, L to yield

$$t - t_0 = \frac{\rho S_a}{M_w k_r C^* D} \left[\frac{D}{C_I^{n-1}} (L - L_0) + \frac{k_r}{2S_a} (L^2 - L_0^2) \right] \quad (15)$$

Equation (15) is then rewritten in terms of weights to better correlate with the TGA experimental data. By substituting $W = \rho AL$ (where W is the mass of the film, and A is its surface area),

$$t - t_0 = \frac{S_a}{M_w k_r C_I^{n-1} C^* A} (W - W_0) + \frac{1}{2DM_w C^* \rho A^2} (W^2 - W_0^2) \quad (16)$$

or

$$\frac{t - t_0}{W - W_0} = \frac{\tau_R}{W^*} + \frac{\tau_D}{(W^*)^2} (W + W_0) \quad (17)$$

where $\frac{\tau_D}{(W^*)^2} = \frac{1}{2M_w C^* D \rho A^2}$ and $\frac{\tau_R}{W^*} = \frac{S_a}{M_w K_r C_I^{n-1} C^* A}$; τ_D and τ_R are the diffusion and reaction times, respectively. W^* is a normalized deposited film mass, where

$$W^* = \frac{M_w C^* A}{S_a} \quad (18)$$

Equation (17) is the equation that will be coupled to the experimental data. This equation can be plotted as a straight line $y = mx + b$, where

$$y = \frac{t - t_0}{W - W_0} \quad m = \frac{\tau_D}{(W^*)^2} \quad x = W + W_0 \quad b = \frac{\tau_R}{W^*}$$

W^* , τ_D , and τ_R can be estimated from the slope m and the intercept b .

Experimental Results

Data were obtained from the TGA experiments and surface analyses of the films; the data were then analyzed to validate the proposed model.

Thermogravimetric Analysis (TGA)

Figure 5 represents typical TGA data obtained during a VPL experiment using a TBPP precursor. As the deposited film grows on the cast-iron substrate, the increasing mass of the substrate is plotted against temperature and time. The isothermal data was statistically analyzed after each TGA experiment before proceeding with the kinetic analysis.

The kinetic and transport parameters were obtained by the least-squares method. The transition from the reaction control regime (constant ordinate) to the diffusion control regime (linear correlation) was determined via one-sided sensitivity analysis. This analysis is illustrated in figure 6. This analysis enabled the identification of what section of the data can be used to estimate each parameter in equation (17).

Typical reaction and transport parameter values calculated from the analysis of the TGA data are summarized in table I. The characteristic diffusive times τ_D are at least 4 orders of magnitude smaller than the characteristic reaction times τ_R (where ε_τ is the calculated error associated with each characteristic time constant), which supports the pseudo-steady-state assumption made in the model formulation.

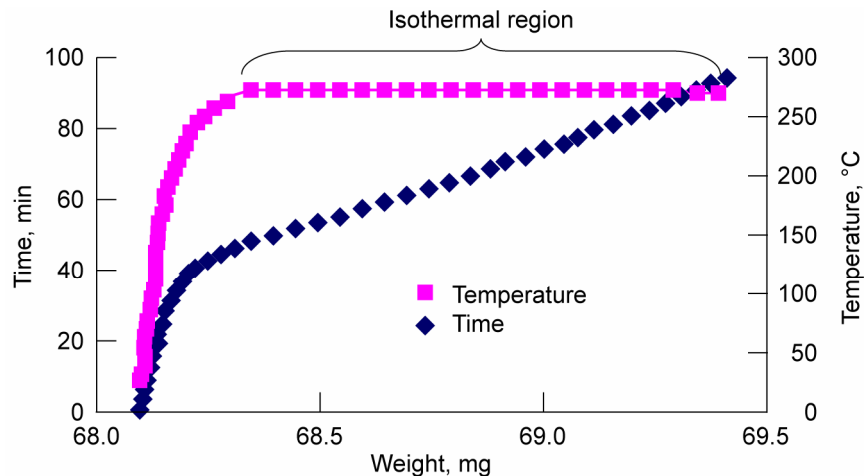


Figure 5.—Typical TGA data with tert-butylphenyl phosphate (TBPP) as precursor, showing isothermal region.

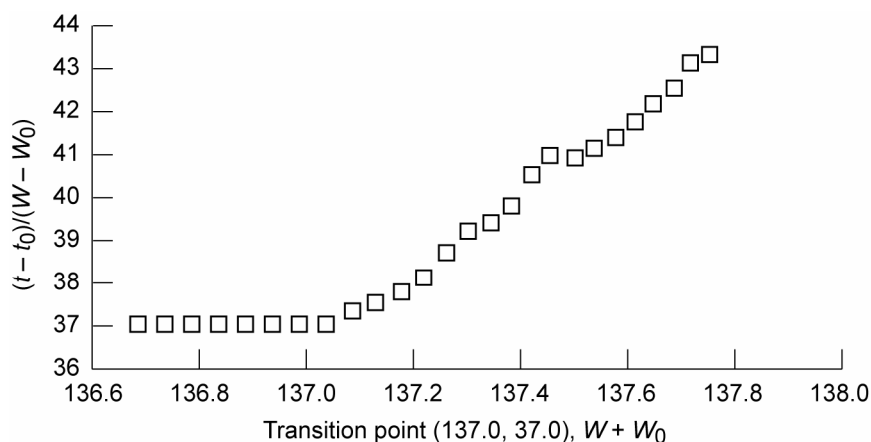


Figure 6.—Identifying the “transition” point through one-sided sensitivity analysis, where W_0 and W are the initial and final film masses corresponding to times t_0 and t , respectively (see eq. (16)).

TABLE I.—TRANSPORT AND KINETIC PARAMETERS
FOR TGA DEPOSITION EXPERIMENTS

Experiment	Temperature, °C	Precursor lubricant mass, g	Film mass, ^a W^* , 10^5 g	Reaction time, τ_R , 10^4 s	Error, ϵ_{τ_R} , 10^4 s	Diffusion time, τ_D , 10^9 s	Error, ϵ_{τ_D} , 10^9 s
1	269.3	0.015	2.0	7	0.4	9	2
2	270.2	0.016	2.1	8	0.3	4	0.5
3	287.9	0.023	3.0	7.4	0.3	9	1
4	308	0.038	4.7	6	0.3	17	2

^a W^* is normalized mass of deposited film, see eq. (18).

TABLE II.—EDXA RESULTS FOR SOLID FILMS DEPOSITED
ON CAST IRON FOILS FROM TBPP PRECURSOR
[Values expressed in atomic percent.]

Element	Control (before deposition)	After deposition for 30 min at			
		275 °C	280 °C	290 °C	330 °C
C	0	9.44	10.32	12.06	14.07
O	0.94	10.36	11.97	14.52	23.9
P	0	0.43	0.83	1.1	3.81
Fe	99.06	79.76	76.89	72.32	58.22

Energy Dispersive X-Ray (EDXA)

The films deposited on cast-iron substrates were characterized by EDXA. Table II shows the EDXA results for films obtained at different temperatures.

The results suggest that as the deposition temperature increases, a thicker film is created. For example, for the same amount of lubricant used at 275 and 280 °C, the phosphorus concentration in the films approximately doubled. Also, for experiments from 290 to 330 °C the amount of phosphorus increased three and a half times, while the lubricant mass was only 25 percent larger at these temperatures.

Auger Electron Spectroscopy (AES)

Film chemistry was investigated with AES. Figures 7 and 8 present profiles of atomic percentages of the element composition of films deposited at low and high temperatures, respectively. These figures show the atomic percentages of carbon, oxygen, iron, and phosphorus as a function of depth. For a 16-mg sample of lubricant used for deposition experiments at 270 °C, the phosphorous atomic percentage becomes negligible after 135 nm. However, for films deposited at 290 and 310 °C from 26 mg of lubricant, the amount of phosphorous remains noticeable up to depths of 225 and 720 nm, respectively. There is a small amount of carbon in the outer layer of each of those samples. Artifacts resulting from the low sensitivity of the AES to phosphorous and from noise in the spectrum are more noticeable as the atomic percentage of phosphorous becomes smaller.

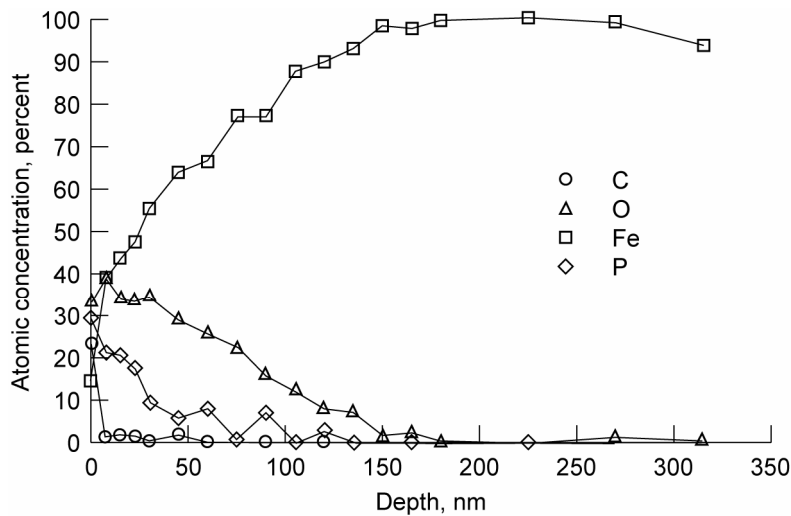


Figure 7.—Auger electron spectroscopy depth profiling for solid lubricant film deposited on cast iron at 270 °C from TBPP precursor.

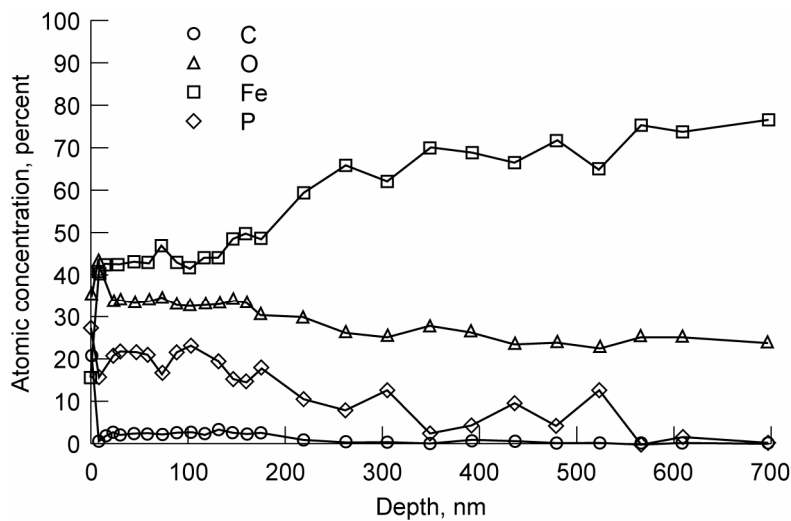


Figure 8.—Auger electron spectroscopy depth profiling for solid lubricant film deposited on cast iron at 310 °C from TBPP precursor.

Fourier Transform Infrared Spectroscopy (FTIR)

The main functional groups in the deposited film surface were identified by FTIR. Figure 9 shows the spectrum for a film deposited at 275 °C. The sloping baseline observed in the spectra is a result of surface roughness and reflectivity difference between the gold slide used as a background and the cast-iron substrate. Spectra for foils treated below 275 °C appear similar to that of bare cast-iron, which would suggest that these experiments resulted in the thinnest films reported.

The spectra for experiments where successful deposition occurred did not show any aromatic C–H stretches, which indicates that the outermost film layers do not have any aryl groups. This means that either the TBPP decomposes while being heated and only the phosphate anion PO_4^{3-} reacts with the iron surface or that TBPP molecules reach the iron surface and upon reaction the aryl groups decompose. As the deposition temperature increased, the P=O peak becomes more prominent. In addition, an extra peak corresponding to P–O–C becomes visible as the temperature increases (fig. 10). These observations corroborate the AES analysis that as the deposition temperature increases, thicker films are generated.

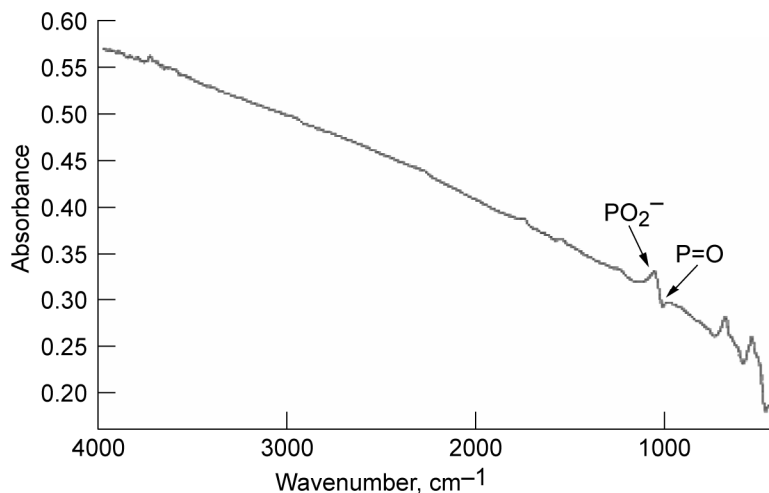


Figure 9.—Infrared spectrum of solid lubricant film deposited on cast iron at 275 °C from TBPP precursor.

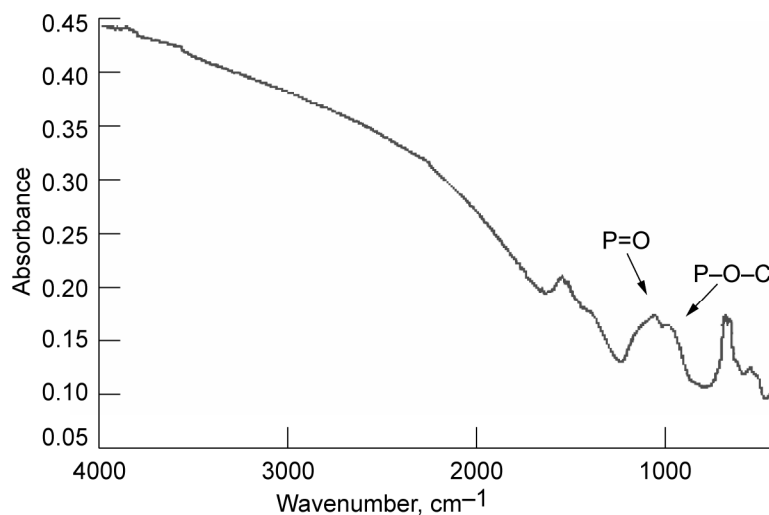


Figure 10.—Infrared spectrum of solid lubricant film deposited on cast iron at 310 °C from TBPP precursor.

Conclusions

In order to better understand the vapor-phase lubrication mechanism, a pseudo-steady-state mathematical model of the deposition process was formulated, and an equation was derived relating kinetic and transport parameters to the deposited film growth.

A modified thermogravimetric analysis (TGA) unit then was successfully used to grow solid lubricious films on cast-iron foils by chemical vapor deposition. These deposition experiments produced films at temperatures ranging between 270 and 330 °C using tert-butylphenyl phosphate as a precursor. The modified TGA unit enabled deposition experiments under a controlled atmosphere and at constant temperature. Studies were restricted to the temperature range that has shown 1 order of magnitude reductions in the coefficient of friction for dynamic lubrication processes.

The experimental data collected in this temperature range were used to estimate the kinetic and transport parameters involved in the deposition. Surface analysis of the deposited films revealed the temperature dependence of the deposition mechanism. The ability to carry out deposition experiments under controlled temperature conditions yielded reliable estimations of the temperature dependence of transport and kinetic parameters. The numerical values of the transport and kinetic parameters validated the pseudo-steady-state assumption made in the development of the mathematical model. This model can now be used as a predictive and scale-up tool for future vapor-phase lubrication studies.

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13. ABSTRACT (Maximum 200 words) One of the major problems preventing the operation of advanced gas turbine engines at higher temperatures is the inability of currently used liquid lubricants to survive at these higher temperatures under friction and wear conditions. Current state-of-the-art organic liquid lubricants rapidly degrade at temperatures above 300 °C; hence some other form of lubrication is necessary. Vapor-phase lubrication is a promising new technology for high-temperature lubrication. This lubrication method employs a liquid phosphate ester that is vaporized and delivered to bearings or gears; the vapor reacts with the metal surfaces, generating a solid lubricious film that has proven very stable at high temperatures. In this study, solid lubricious films were grown on cast-iron foils in order to obtain reaction and diffusion rate data to help characterize the growth mechanism. A phenomenological mathematical model of the film deposition process was derived incorporating transport and kinetic parameters that were coupled to the experimental data. This phenomenological model can now be reliably used as a predictive and scale-up tool for future vapor-phase lubrication studies.				
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